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Investigation of Discrimination Enhancement in Polysilsesquioxane Based Positive Resist for ArF Lithography

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ABSTRACT

In order to establish surface imaging process using O₂-RIE on ArF lithography, silicon containing bi-layer resists have been investigated. We synthesized cyclohexyl pendant silsesquioxane polymer to obtain high transparency at ArF wavelength. This polymer has ladder siloxane structure with high Si density (13 wt%), over 80%/@0.35um transmittance at 193nm, and has carboxylic acid partially protected by acid labile group for TMAH aq. development.

Addition of base enhanced the slope of deprotecting reaction and suppressed acid diffusion. The function of specific amines as acid quencher was considered to cause "Proton-Jumping".

Substituting of carboxylic acid by alcohol type polar linkage increased alkali tolerance, adhesion force and polymer Tg. Standard 2.38wt% TMAH developer was applied and expanded the dissolution rate gap. For further improvement of the resolution, we increased alkali tolerance by introduction of tricyclodecanyl pendant and optimized alkali concentration of developer. As a result, suitable dissolution curve for surface imaging resists was realized and rectangular patterns were observed on bottom ARC.

Keywords: 193 nm lithography, bi-layer, surface imaging, silsesquioxane, ArF, O₂-RIE

1. INTRODUCTION

To date, various silicon containing resists have been investigated for bi-layer process. Among them, silsesquioxane polymer based on ladder siloxane structure^{1,2,3,4,5)} was expected to be suitable for superior O₂ dry etching resistance⁶⁾. Especially, benzyl-pendant silsesquioxane polymer was considered attractive by having a potential for high resolution.

As the first version, we examined p-hydroxybenzyl-pendant silsesquioxane polymer that had partially blocked by acid labile protecting group R, for KrF lithography.

However, benzylpendant polysilsesquioxane based resist has very strong absorption at 193nm, and was far from rectangular pattern even if less than 1000A thickness. For improvement of CD control accuracy, perpendicular side wall profiles are essential also in bi-layer resist. Fundamentally, raising transmittance and discrimination enhancement in dissolution curve are effective techniques among the keys to advanced resist system.

To increase the transmittance at 193nm, we tried to introduce alicyclic compound moiety into silsesquioxane structure. A new cyclohexyl-pendant silsesquioxane polymer was synthesized as 2nd version. Alicyclic moiety had made it possible to achieve all of the requirements, such as transparent improvement, narrow Mw dispersion and regular ladder structure by moderate steric hindrance.

To enhance the discrimination curves on dissolution rate, it is necessary to enhance the discrimination on deprotecting reaction and the discrimination on acid generation. It is well known technique that addition of small amount of base in chemical amplified resist improve the pattern profiles, resolution, depth of focus, post exposure delay (PED) stability and substrate stability^{7,8,9,10}.

We surveyed the applicable base, focused on contrast enhancement effect in deprotecting reaction slope. In this study, we report that neutralization model leads to steep curve of acid concentration by addition of small amount of base. This non-linear acid generation improves the discrimination slope of deprotection reaction. We call this steep acid generating phenomenon "Proton-Jumping".

Next issue would be dissolution enhancement in alkali developer. We found that slope in the low dissolution range strongly influenced to pattern resolution, whereas the big dissolution rate difference between exposed and unexposed area is less important for thin surface imaging resists. Introduction of polar linkage with hydroxy groups to carboxylic acid improves the slope on dissolution rate. The hydroxyl groups reinforced alkali tolerance, adhesion force to substrate and polymer Tg (Ver.3). Finally, in Ver.4 polymer, hydroxy-tricyclodecanyl type pendant was introduced to increase its alkali tolerance.

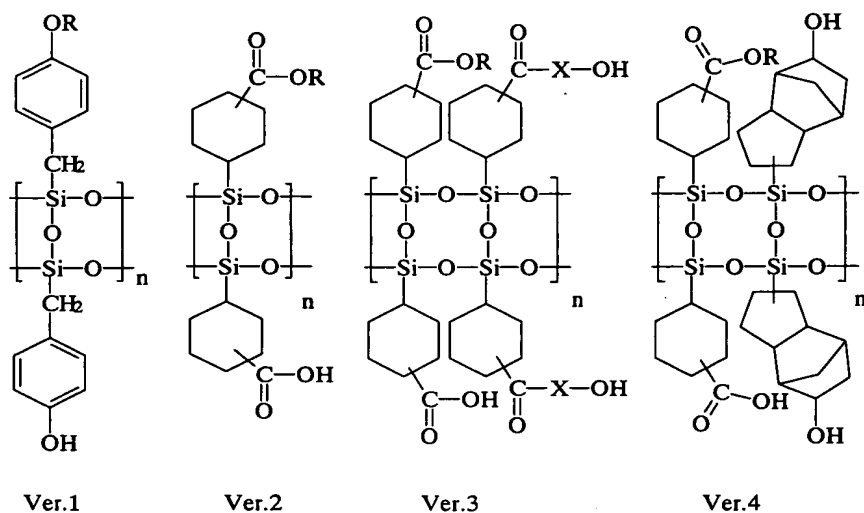


Figure 1 Structure of the Polysilsesquioxane

3 Experimental

3.1 Lithography

3.1.1 Resist Formulation

Polysilsesquioxane and 2wt% PAG for polymer and 20molar % of amine for PAG were dissolved in propylene glycol 1-monomethyl ether 2-acetate(PGMEA) and the solution were filtered through 0.2-micron Teflon filters.

3.1.2 Resist Processing

The resist was coated by Track system and baked at 100°C for 90 seconds to get a nominal resist thickness of 0.15-0.35 μ m. The resist thickness was measured by Ramda Ace VL-M8000-S: Dainippon Screen Manufacturing thickness gauge using a refractive index of 1.48. Exposure were carried out on a Nikon ArF excimer stepper with NA0.55 lens and

conventional chrome mask. After exposure, PEB was performed at 100°C for 90 second. The wafers were developed stationary puddle for 60 second with 0.12-2.38wt% tetramethylammonium hydroxide (TMAH). The cross sectional resist profiles were obtained by a Hitachi S4100 SEM.

3.2 Transmittance of Polymer films

Polysilsesquioxane was dissolved in propylene glycol 1-monomethyl ether 2-acetate(PGMEA), and was coated on synthesized quartz wafers and pre-baked on the same condition as on Si wafers.

Vacuum ultra violet wavelength spectrometer VUV-200S: Nipponbunko was applied for measuring transmittance of polymer films.

3.3 Molecular weight and Dispersion of Polymer

Molecular weight and dispersion of polymer were measured on Gel permeation chromatography HLC-8020: Tosou in THP solvent. And it was converted to standard molecular weight of polystyrene.

3.4 Thermal Analysis of Polymer Films and Resist Films

Differential Scanning Calorimeter: DSC-8230 RIGAKU was applied for measuring Tg. Thermal flow stability was tested by heating pattern formed wafers. Side wall of 1um width pattern profiles were observed by cross sectional SEM.

3.5 Dissolution Rate Monitoring

Exposure were carried out on KrF excimer laser stepper without masks. ArF exposure were carried out on photochemical analyzer ARFES3000: Lithotech Japan. After exposure, PEB was carried out by Track system and dissolution rate monitoring(Lithotech Japan : MODEL780MK-2) was applied.

3.6 Deprotecting Analysis

Exposure were carried out on KrF excimer laser stepper without masks. After exposure, PEB was carried out by Track system and IR spectrometer JIR-5500: JEOL was applied for measuring an absorption spectrum of acid labile substitution group:R.

4 Result and Discussion

4.1 Characteristics of Polysilsesquioxane

GPC chart is shown in Figure 2. Molecular weight of each polymer was around 3000-5000, dispersion of molecular weight: Mw/Mn were controlled around 1.5.

Molecular weight, dispersion and glass transition temperature were summarized in Table 1.

Polymer Version	Protection Ratio R (%)	Protection Ratio -OH (%)	MW	Mw/Mn	Tg (°C)	Thermal Flow (°C)
Ver. 1	35	-	3000	1.4	120	120
Ver. 2	60	-	3000	1.6	100	110
Ver. 3	60	20	3000	1.6	100	110
Ver. 4	40	45	4000	1.4	120	120

Table 1 Summary of polymer characterization

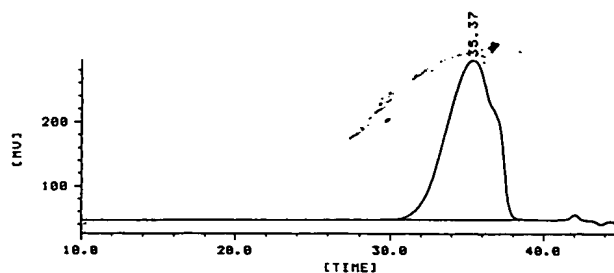


Figure 2 GPC Chart of Polysilsesquioxane

Figure 3 shows transmittance of cyclohexyl pendant type polymer and contained 2wt% PAG resist. Over 80% transparency was obtained in 0.35 μ m thickness at 193nm. In version 3 and 4 polymer, transmittance decrease to around 68% and 58% , respectively (Figure 4).

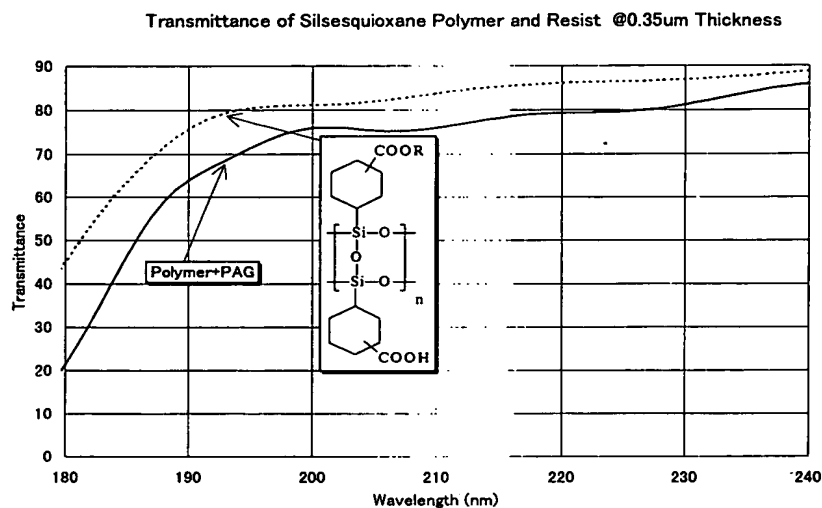


Figure 3 Transmittance of Ver.2 polymer and 2% PAG contained resist

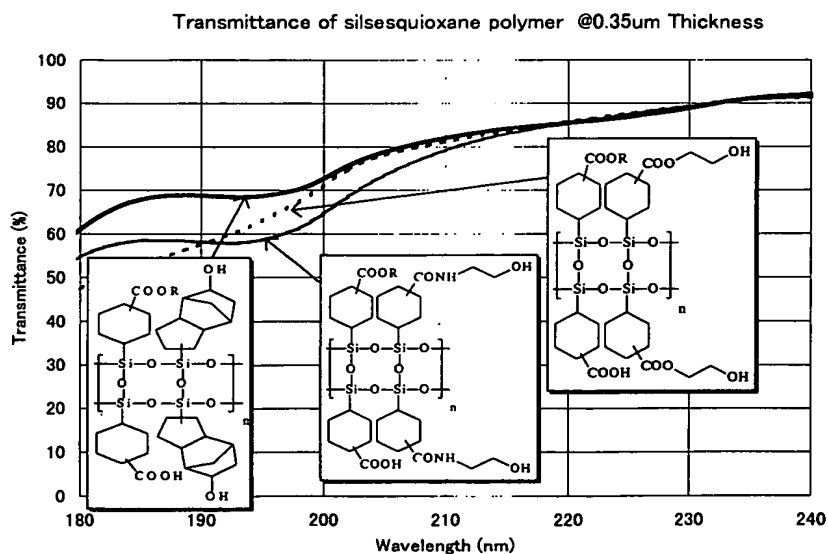


Figure 4 Transmittance of Ver.3 and Ver.4 polymer

4.2 Proton-Jumping Theory and Calculation

Photo-generating acid concentration was measured using tetrabromophenol blue disodium salt as a indicator of acid at KrF exposure and rate constant C: 0.03 was obtained with fitting in equation (2).

Photo-generated acid and additive base attained equilibrium with constant : K.

Neutralization model of acid by additive base was explained the effective acid concentration to cause deprotecting reaction. Effective acid was calculated to α in Eq. (4). In the larger value of k, acid concentration change more rapidly at equivalent point (Figure 5).



H^+ : Photo-generated Acid

B : Additive Base

$$X_0 = 1 - \exp C \cdot E \quad (2)$$

$$K = \frac{X_0 - \alpha}{\alpha (B_0 - X_0 + \alpha)} \quad (3)$$

$$K \alpha^2 + (B_0 K - X_0 K + 1) - X_0 = 0 \quad (4)$$

$$\alpha = \frac{-(B_0 - X_0 K + 1) + \sqrt{(B_0 - X_0 K + 1)^2 + 4 X_0 K}}{2K} \quad (5)$$

C : Photo acid generation constant

E : Dose (mJ/cm^2)

$K = [\text{BH}] / [\text{H}^+][\text{B}]$ Equilibrium constant

X_0 : quantity of photo generated acid

B_0 : quantity of additive base

α : quantity of acid with equilibrium state

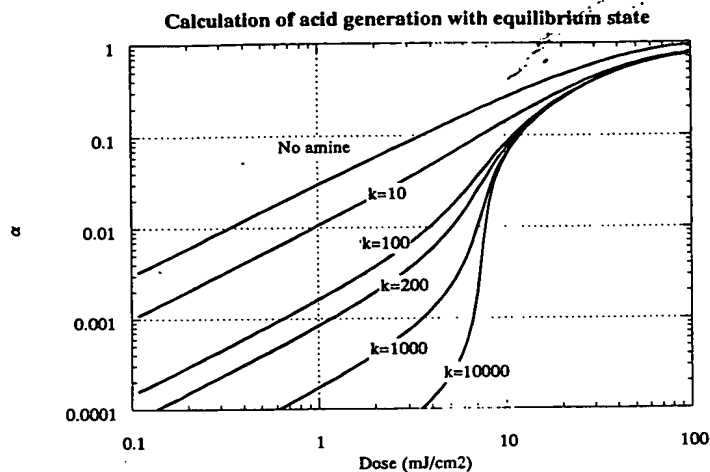


Figure 5 Calculation of Proton-Jumping

Rate constant and order of deprotecting reaction were calculated in equation (6)¹¹⁾. In the case of no base, K is 1 and B_0 is zero, in equation (2). K_d and m_d were obtained from curve fitting on IR analysis of acid labile substitution group: R. Using K_d and m_d values, in the case of base addition, equilibrium constant : K was estimated to about 1000 (Figure 6).

$$R = \exp(-k_d \cdot T \cdot \alpha^{m_d}) \quad (6)$$

R : Protection Ratio (1/100%)

K_d : Reaction constant in deprotection

T : PEB time (sec.)

m_d : Reaction order in deprotection

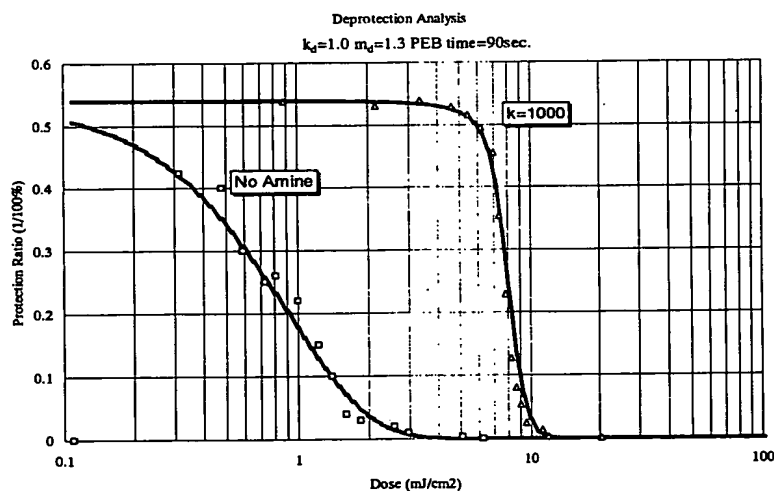


Figure 6 Fitting calculation and analysis of deprotecting reaction

Disadvantage of proton-jumping system by acid quencher is sensitivity reduction. The more high speed resist are required in ArF lithography to avoid lens material's compaction. As shown in Figure 7, in the case of minimum quantity (10~20 molar % of PAG) of base, sensitivity remained within several times reduction. Further, ArF sensitivity is higher than KrF exposure in Figure 8. Sensitivity reduction by base additives is not considered as conclusive problem.

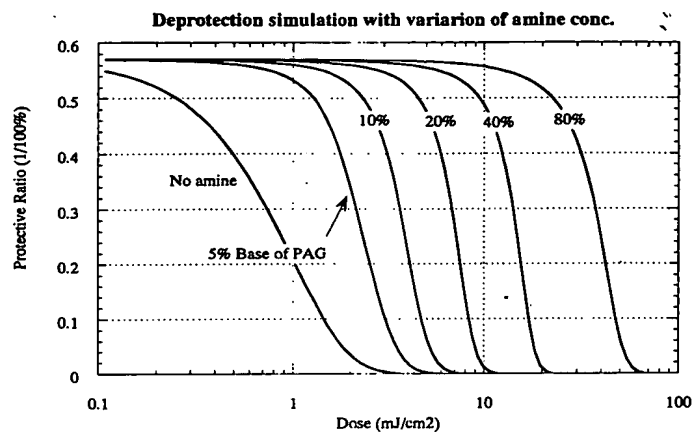


Figure 7 Deprotecting calculation with Variation of base quantity

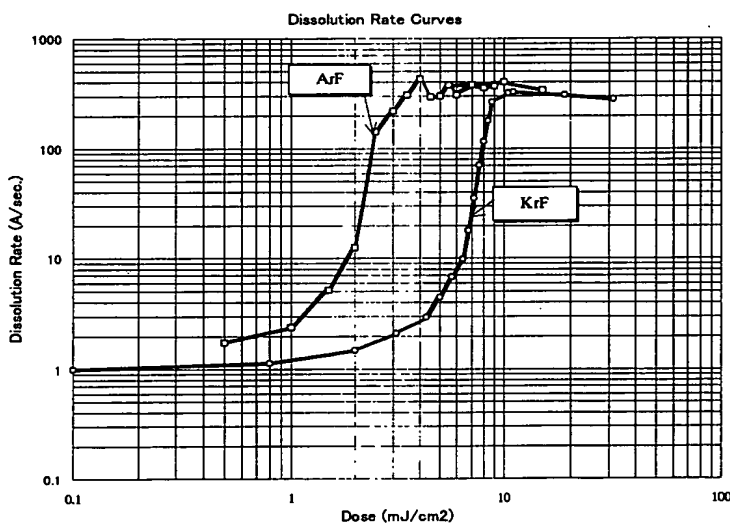


Figure 8 Difference of sensitivity KrF and ArF

4.3 Dissolution Characteristic and Lithographic Evaluation

To obtain steep slope in dissolution rate curve, both deprotection and dissolution should start at a same dose. Benzyl-pendant type polysilsesquioxane showed identical dose for each other, and successfully enhanced the discrimination (Figure 9,10). Furthermore, resolution and pattern profiles were improved in 1.90 weight % TMAH development.

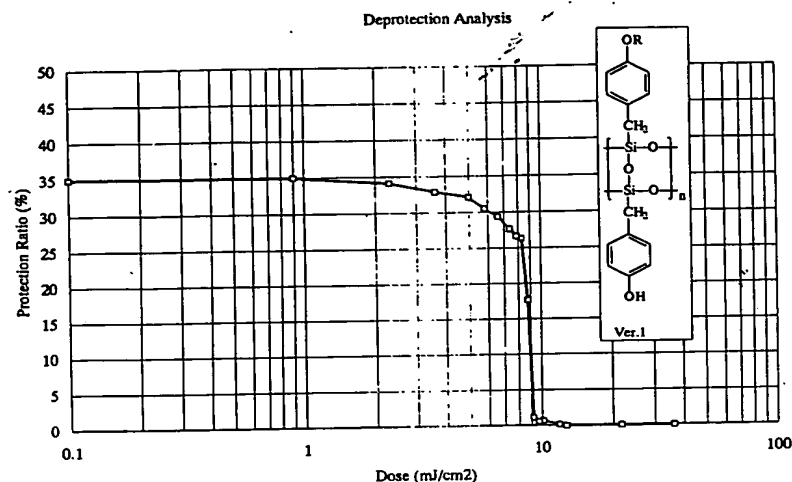


Figure 9 Deprotection Curve of Ver.1 Resist

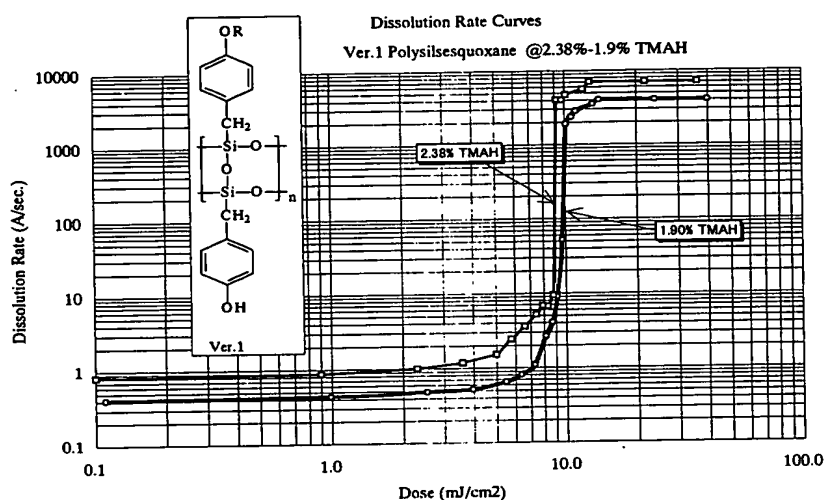


Figure 10 Dissolution Curves of Ver.1 resist in 2.38 and 1.90wt% TMAH

Relationship of dissolution curve and deprotecting reaction in Ver.2 resist are shown in Figure 6 and 11. They showed identical dose for each other. However, dissolution slope in the range 1-10 Å was poor. We related slope in the range of slower dissolution to resist pattern formation, especially in thin surface resist.

Pattern profiles of Ver.2 resist are shown in Figure 13. Resolution and pattern shape must be improved still more.

Standard 2.38 weight % TMAH was applied for Ver.4 resist and expanded dissolution gap. But, resolution was inferior to Ver.2. In 2.38% TMAH developing, resist dissolve smaller dose than Proton-Jumping, so dissolution slope in the range 1-10 was very poor. The cause of dissolution at smaller dose than proton-jumping point was considered high solubility of carboxylic group. In Ver. 4 resist, the slope in the range 1-10 Å was improved by employing diluted developer (Figure 12).

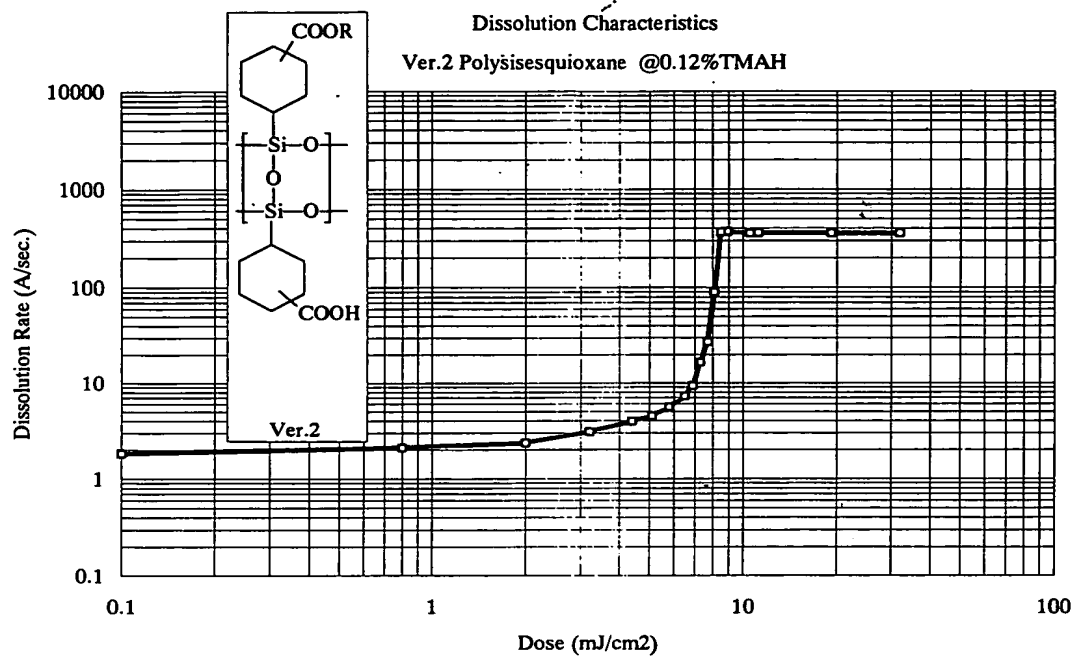


Figure 11 Dissolution Curve of Ver.2 resist in 0.12wt% TMAH

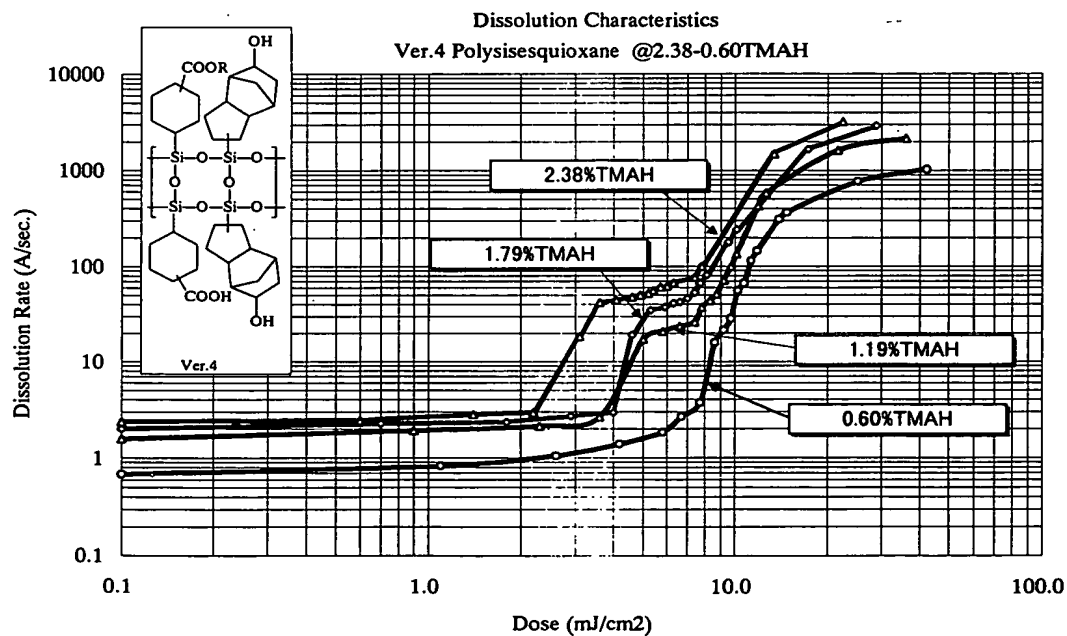


Figure 12 Dissolution Curves of Ver.4 resist in 2.38-0.6wt% TMAH

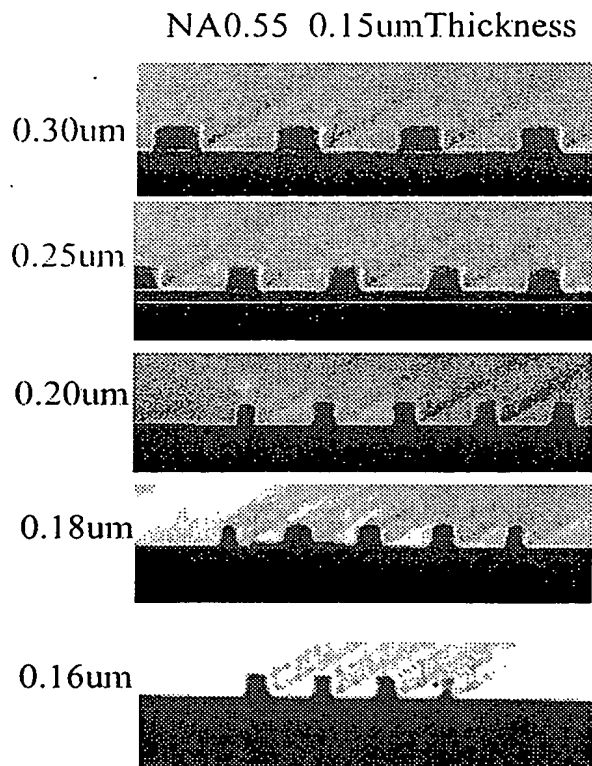


Figure 13 Pattern profiles in Ver. 2 Resist with 0.12%TMAH Development
These pictures presented by ASET.

5 Conclusion

Alicyclic pendant polysilsesquioxane with carboxylic acid partially protected by acid labile group was synthesized. Addition of base enhanced deprotecting discrimination by Proton-Jumping. Diluted TMAH developer enhanced the dissolution rate slope and improved the resolution. Particularly, hydroxytricyclodecanyl pendant polysilsesquioxane shows excellent steep slope.

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